

CARBON DEPOSITION ON Fe, Ni, AND Cr AND THEIR ALLOYS IN SUPERCRITICAL JET FUEL ENVIRONMENT

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INTRODUCTION

The formation of carbon deposits on metal surface from decomposition of jet fuel is a major concern in the development of advanced aircraft in which the fuel is also used as a heat sink (1). Metal surface composition can strongly affect carbon deposition from thermally stressed jet fuel or model hydrocarbon (2). Carbon deposition on heat exchanger surfaces, filters, injectors and control valves can pose serious operational problems. Depending on the temperature and pressure of the system and the activity of metal surfaces, the deposition may be catalyzed by metal surfaces with the formation of filamentous carbon, or other forms of carbonaceous solids (3, 4).

A considerable volume of research has been carried out on Fe and Ni containing catalysts/or alloys over the past two to three decades to investigate their catalytic activity for the formation of carbonaceous deposits from various hydrocarbons under different conditions (5-7). Jet fuels may contain up to 2000 ppm sulfur that can have a significant effect on solid deposit formation from thermal stressing of fuels on metal surfaces. The effects of sulfur compounds on carbon deposition are not clear. Ohla and Grabke (8) reported that sulfur retarded graphitic carbon formation on iron, but the growth of graphitic carbon on nickel was accelerated by sulfur. Trimm and Turner (9) observed both the facilitation and retardation effect of sulfur on carbon deposition from a mixture of propane and hydrogen on pre-sulfided nickel, copper, iron and stainless steel surfaces. They suggested that the formation of stable metal sulfides on surfaces inhibit carbon deposition, whereas the formation, and subsequent decomposition of labile metal sulfides accelerated the deposition process.

The main objective of this study is to investigate and characterize the carbon and sulfur based solid deposit formation from jet fuel (JP-8) stressing on pure Ni, Fe and Cr and binary alloys of Fe/Ni (55/45), Fe/Ni (64/36) and Ni/Cr (80/20) surfaces.

EXPERIMENTAL

Thermal stressing of a JP-8 fuel (120 ppm constituent sulfur) was carried out in the presence of pure Ni, Fe, and Cr and Fe/Ni (55/45), Fe/Ni (64/36), and Ni/Cr (80/20) foil surfaces. The 15x0.3x0.01 cm coupons were placed at the bottom of a 20 cm, 0.63 cm (O.D) and 0.4 cm (I. D.) glass-lined tube reactor. The reaction system was heated to 500°C for 2 hours under argon flow at 500 psig prior to the introduction of the JP-8. Then, the preheated fuel at 250°C was introduced to the reactor. The reactor temperature and the fuel pressure were kept constant throughout the experiments at 500°C, and 500 psig, respectively. The flow rate of jet fuel was maintained at 4 ml/min. After 5 hours of stressing, the foils were cooled down under argon flow in the reaction system.

The stressed foils were analyzed using LECO-RC412 Multiphase Carbon analyzer to determine the total amount of carbon deposition on the foils as well as temperature programmed oxidation (TPO) burn-off profiles (10). In TPO experiments, the CO₂ evolution was measured by two IR cells as a function of time while heating the sample from 100°C to 900°C at a constant rate of 30°C/min under O₂ flowing at 750 ml/min. The carbon deposits were also examined by field emission SEM (FESEM), SEM with energy dispersive x-ray spectroscopy (EDS), and x-ray diffraction (XRD).

RESULTS AND DISCUSSION

As shown in Table 1, the thermal stressing of JP-8 fuel on Ni and Fe and their alloys resulted in large amounts of carbonaceous solid deposits as compared to Cr and binary alloy with Ni, Ni/Cr (80/20). Total amounts of deposits were measured by using the LECO multi-phase carbon analyzer and the results were calculated in terms of μg of carbon per cm^2 surface area of the metal foil. The amount of carbon deposited on pure Ni, and Fe surfaces is 100, and 132 $\mu\text{g}/\text{cm}^2$,

respectively. The two binary alloys of Fe and Ni (with a relatively small difference in their bulk compositions) collected substantially different amounts of deposits. The alloy with 55% Fe and 45% Ni collected 55 $\mu\text{g}/\text{cm}^2$ carbon deposit (lower than that collected on pure Fe, or Ni), whereas 64% Fe and 36% Ni collected 389 $\mu\text{g}/\text{cm}^2$ (much higher than that collected on either pure metal surface). As expected, the addition of Cr to Ni reduced the deposit formation significantly. The binary Ni/Cr alloy collected 6 $\mu\text{g}/\text{cm}^2$ carbon deposit.

Table 1. The amount of carbon deposits collected on Ni, Fe, Fe/Ni (55/45), Fe/Ni (64/36), and Ni/Cr (80/20) surfaces. JP-8 was thermally stressed at 500°C and 500 psig for 5h at a flow rate of 4 ml/min.

Metal	Amount of deposit ($\mu\text{g}/\text{cm}^2$)
Ni	132
Fe	100
Fe/Ni (55/45)	55
Fe/Ni (64/36)	389
Ni/Cr (80/20)	6

Figure 1 shows the SEM micrographs of deposits formed from JP-8 stressing at 500°C on pure Ni, and Fe surfaces. In Figure 1a, it is seen that Ni surface is completely covered with filamentous deposits formed all over the surface. Most of the filaments have twisted shapes and they are longer than 5 μm in length. High magnification images from FESEM examination showed that some of the filaments contain metal particles at their tips. An EDS elemental map analysis indicated that the surface contains high concentrations of sulfur in addition to carbon. The sulfur compounds present in jet fuel such as, thiophene and benzothiophene and their alkylated homologs appear to react with metal surfaces at high rates. An XRD analysis clearly showed the formation of Ni_3S_2 on the nickel surface upon stressing with JP-8.

The thermal stressing of JP-8 at 500°C on pure Fe surface produced two different sulfur-containing structures besides the carbon deposits. Figures 1b and 1c show hexagonal, tetragonal and monoclinic structures of Fe_{1-x}S , pyrrhotites, and FeS, troilite formed on pure Fe surface. In Figure 1b, a carbon deposit in amorphous form was also observed as bright overlayer between the sulfide crystals. There was no filamentous deposit observed on the Fe surface. The formation of highly crystalline sulfide structures may inhibit the catalytic effect of Fe surface to form carbon filaments. Trimm and Turner (9) also observed similar behavior during propane stressing in the presence of H_2S on the Fe surface. The authors reported that the Fe surface did not produce much carbon deposit when H_2S is present, but without H_2S , the Fe surface collected a significant amount of carbon deposit.

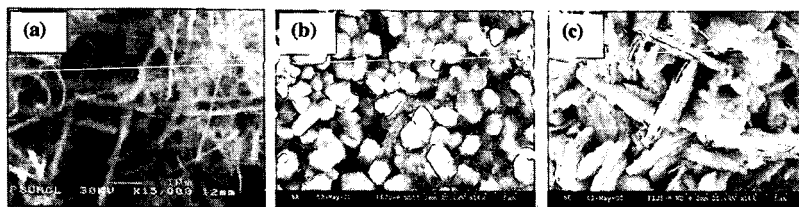


Figure 1. SEM micrographs of carbon deposits from thermal stressing of JP-8 at 500°C and 500 psig for 5h at flow rate of 4 ml/min on Ni (a), and Fe (b and c) surfaces.

Figures 2a, 2b and 2c show carbon and sulfur deposit structures on binary alloys of Fe/Ni (55/45), Fe/Ni (64/36) and Ni/Cr (80/20). No distinctive filamentous carbon morphology was observed on the surfaces of the deposited coupons. The deposits on the two Fe/Ni binary alloys appeared to have particulate morphologies with different surface coverage and particulate size. The bright carbon deposit structures seen on the Fe/Ni (55/45) surface in Figure 2a covered the whole alloy surface. The average particulate size of the deposits is 0.2 μm . However, on the Fe/Ni (64/36) shown in Figure 2b, deposits collected more on isolated areas without covering the surface completely. The average size of the particulate deposits is 0.5 μm , larger than that observed on the other binary Fe/Ni alloy. From these observations and the TPO results, one can suggest that the Fe/Ni (64/36) alloy has a higher activity towards carbon deposition than the Fe/Ni (55/45) alloy. This difference in surface activity can be attributed to differences in surface composition and metallic phases present in these alloys among other factors, such as

impurities and physical characteristics of the alloy surfaces. Figure 2c shows that addition of Cr to Ni significantly reduced the surface activity towards sulfur and carbon corrosion. A relatively small amount of deposits observed on the surfaces consist of sulfide flakes and small particles of solid carbon.

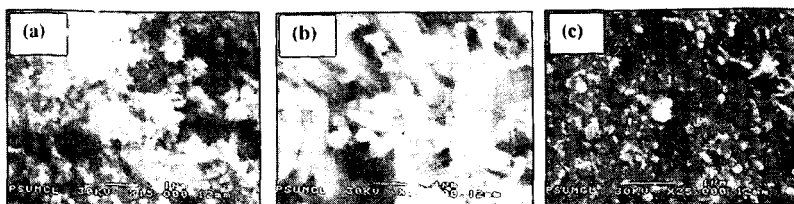


Figure 2. SEM micrographs of carbon deposits from thermal stressing of JP-8 at 500°C and 500 psig for 5h at flow rate of 4 ml/min on Fe/Ni (55/45)(a), Fe/Ni (64/36) (b) and Ni/Cr (80/20) (c) alloy surfaces.

The TPO profiles shown in Figure 3 indicate that on the pure Ni surface there are mainly two types of deposit structures that exhibit different reactivities in oxygen, giving two CO₂ evolution peaks centered at 375 and 750°C, respectively. The lower temperature peak can be attributed to reactive deposits, such as disordered, or amorphous deposits, and metal carbide (Ni₃C) particles. The higher temperature peak, on the other hand, should result from the oxidation of more ordered, e.g., graphitic, structures, produced around the metal particles in filamentous carbon structures.

On the Fe surface, three peaks were observed at 150, 275 and 450°C burn-off temperatures. The first low temperature peak can be related to the evaporation of trapped hydrocarbon molecules in the porous deposit structure, and the second broad peak results probably from the highly reactive carbon deposits formed between the sulfide crystals (Figure 1b). The third peak that appeared at around 450°C can be attributed to the oxidation of different iron carbides, e.g., Fe₃C₂, Fe₃C, and FeC, or of the more ordered carbon deposits formed on metal surfaces. No carbides were identified by XRD, probably because their quantity is very small compared to that of sulfides on the Fe surface.

The TPO profiles of the binary alloys of Fe and Ni are also shown in Figure 3. The heavy deposition on Fe/Ni (64/36) alloy is particularly noteworthy. The three major TPO peaks of the deposited alloys appeared at 150, 250-300 and 400°C. It is interesting that the high temperature peak (750°C) seen on the deposited nickel surface is absent on the deposited alloy surfaces. Similar to pure Fe TPO profiles, the first two peaks of alloys can be ascribed to the evaporation and oxidation of the trapped hydrocarbons, and the oxidation of the highly reactive solid deposits. The third very sharp peak at 400°C, probably results from the presence of an active alloy phase (Fe and Ni), which seems to catalyze the oxidation of the carbon deposits, as well.

As seen in Figure 2c, the amount of deposit on Ni/Cr alloy surface was very low compared to that obtained on Ni/Fe alloys. The TPO profile of the carbon deposits on Ni/Cr surface showed only one broad peak at 375°C that can be attributed to the oxidation of amorphous deposits and metallic carbides of Ni and Cr.

CONCLUSIONS

The catalytic effect of Ni and Fe surfaces resulted in significant amount of carbon deposits during the thermal stressing of JP-8 fuel in a flow reactor producing both filamentous, crystalline, amorphous, and metal carbide deposits. The sulfur compounds in the jet fuel lead to the formation of metal sulfides that cause surface corrosion and increase the surface area available for carbon deposition. The binary alloys of Fe and Ni further increased both carbon and sulfur deposition depending on the Fe content. The Cr addition to Ni, however, inhibited the catalytic activity of Ni significantly compared to the Ni and Fe alloys.

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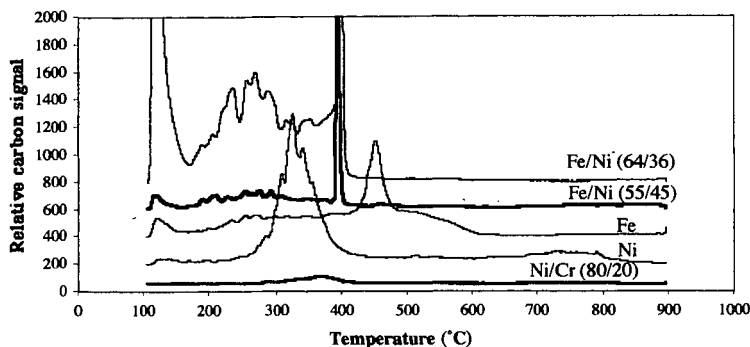


Figure 3. TPO profiles of deposits from JP-8 stressing at 500°C and 500 psig for 5h at a flow rate of 4 ml/min on pure Ni and Fe and Fe/Ni (55/45), Fe/Ni (64/36) and Ni/Cr (80/20) alloys.

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